

Volume 4: Potential Ground and Surface Water Impacts

Chapter 9: Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Future Research

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9. Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Future Research

9.1. Introduction

A comprehensive understanding of the effects of ethanol on the fate and transport of gasoline compounds is needed to determine if the economic and air-quality benefits of adding such fuel alcohols to gasoline outweigh their potential detrimental effects on groundwater pollution and related health risks. An important consideration, which is related to the decision to use ethanol, is the potential effect it may have on the fate and transport of toxic gasoline components (in particular, benzene, toluene, ethylbenzene, and xylenes [BTEX]). For example, while California has implemented improved containment practices for underground storage tanks (USTs), releases of gasoline that may impact ground- and surface-water resources can still be expected. This fate-and-transport information is important for evaluating the impact that ethanol may have on the cleanup of gasoline releases and on California's water resources in general.

The chapters in this volume have summarized the possible release scenarios associated with the use of ethanol as a fuel oxygenate (Chapter 1: Rice *et al.*, 1999), and the effect of ethanol on the fate and transport of BTEX compounds (Chapter 2: Powers and Heermann, 1999) and on their natural attenuation and biodegradation (Chapter 3: Alvarez and Hunt, 1999). We reported the results of the predictive modeling performed to compare BTEX groundwater plumes in the presence of ethanol (Chapter 4: McNab *et al.*, 1999). We considered the potential impacts of the use of ethanol-containing gasoline on surface-water resources (Chapter 5: Layton and Daniels, 1999) and compared possible nonoxygenated fuel formulation to MTBE- and ethanol-containing gasoline (Chapter 6: Marchetti *et al.*, 1999). We evaluated the analytical methods available for the detection of ethanol in the environment (Chapter 7: Koester, 1999). We performed a comparative analysis of potential groundwater resource impacts for gasoline containing methyl tertiary butyl ether (MTBE) or ethanol (Chapter 8: Dooher, 1999).

As a result of the assessment contained in this volume, we have identified important knowledge gaps regarding the anticipated environmental behavior of gasoline containing ethanol. This chapter summarizes those knowledge gaps and provides recommendations for future research that would improve decision-making regarding the use of ethanol in oxygenated and reformulated gasolines in California.

9.2. Knowledge Gaps in the Life-cycle Analysis of Ethanol and Nonoxygenated Fuel Compounds

During the evaluation of ground- and surface-water impacts, we began the development of a comprehensive life-cycle model (Chapter 1: Rice *et al.*, 1999). This life-cycle model systematically addresses impacts from fugitive and accidental releases associated with the

production, distribution, and use of gasoline containing ethanol. Time constraints for producing this particular assessment limited its focus only to those scenarios of chronic or accidental releases of ethanol that are most likely to impact ground and surface waters. Therefore, we were unable to fully consider other scenarios related to releases of substances as a consequence of the transportation and use of feedstocks required for ethanol production as well as from activities conducted at centralized blending centers. Also not considered were the additional implications of agricultural-related impacts from ethanol-fuel production. For example, increased corn-production for ethanol in California and elsewhere will require the application of additional herbicides/pesticides which may impact the environment. Including such scenarios will improve the breadth of understanding concerning the impacts of ethanol use in motor fuels and, therefore, may warrant more complete evaluation in the future.

We also examined the salient environmental properties of alkylates, which are nonoxygenated compounds that are likely to be used in greater amounts in gasoline after an MTBE phaseout. However, the limited analyses conducted were not completed within the context of an integrated life-cycle analysis concerning their production, storage, and use. Alkylates are complex solutions of isoalkanes, and some properties, such as biodegradability, may not be easily extrapolated to all alkylate components. In general, alkylate biodegradation rate is relatively slow compared to other organic compounds, and some components may not biodegrade in reasonable timeframes.

There is no toxicity data on the chronic effects of isooctane in humans. Additionally, cancer risk and reproductive and developmental effects have not been addressed. Surface releases of alkylates, either on water or land, would probably result in the evaporation of most alkylate into the atmosphere. Overall, it appears that alkylates would not affect dramatic changes in the way gasoline behaves in the environment and, thus, in the treatment of accidental releases.

9.3. Knowledge Gaps in Fate-and-transport Processes Associated with the Use of Ethanol as a Fuel Oxygenate

9.3.1 Subsurface Abiotic Processes

Chapter 2 of this volume identified abiotic processes or mechanisms that affect the fate of ethanol and ethanol-gasolines in the subsurface. These processes include infiltration, spreading at the capillary fringe, and leaching of chemicals into groundwater. They can potentially impact the retention and distribution of gasohol (gasoline containing 10% ethanol) or other petroleum products in the unsaturated zone, the size and the shape of a gasoline pool at the water table, and the flux of contaminants from the gasoline to the groundwater.

The extent of our knowledge about these processes ranges from sufficient to inadequate. For example, we now have a relatively large database quantifying the gasoline-water-ethanol partitioning behavior and cosolvency effect. On the other hand, we have very little information on the behavior of an ethanol gasoline as it infiltrates through the unsaturated zone. We used three categories to summarize the level of understanding of each of the abiotic processes or mechanisms affecting the fate and transport of gasoline containing ethanol:

- Sufficient information for prediction.

- Sufficient information for a rough, first-order approximation.
- Insufficient information.

There is substantial knowledge about many of the mechanisms affecting saturated zone transport of gasoline containing ethanol. The net effect of ethanol on the length and longevity of a contaminant plume, however, requires an understanding of each of the steps that define the complete transport pathway. Rather than just deal with each of these steps individually, it is important to understand the complex interrelationships among the processes involved with the ultimate transport of gasoline components to a potential downgradient receptor.

9.3.1.1. Unsaturated Zone

One of the most critical knowledge gaps is the nature of the interaction of groundwater and air (multiphase flow) with ethanol-containing gasoline in the unsaturated zone. The introduction of ethanol affects the migration and distribution of gasoline in the unsaturated zone in two primary ways:

- Capillary forces are reduced, thereby changing multiphase flow characteristics.
- Pore structure of some mineral types is altered by chemical interactions with ethanol.

Table 9-1 summarizes the knowledge level for the mechanisms associated with multiphase flow through the unsaturated zone. In the presence of ethanol, hydrocarbons can enter smaller pore spaces and drain more easily from unsaturated zone soils. This may impact the distributions of residual fuel hydrocarbons in the unsaturated zone and the periphery of free-product pools that may exist. Among the impacts may be the mobilization of existing unsaturated zone contamination. As a result of the reduction in capillary forces, the height of the capillary fringe may also be reduced. The depth and the area of hydrocarbon pool on top of the water table may be altered (although 10% ethanol in gasoline is expected to have a very minor effect). Further, the dehydration of clays and formation of micro-fractures will increase permeability. The importance of these factors in multiphase flow has not been quantified.

Understanding this process is crucial because knowledge gaps about the early stages of the overall flow and transport make adequate prediction of the important impacts of ethanol on BTEX contamination difficult. A high level of predictive uncertainty will remain until the relationship of each step to the overall process is understood sufficiently. Thus, although first-order assessments can be conducted and are widely cited, conclusions drawn from this type of assessment will be applicable to only a small subset of environmental conditions that may be associated with potential releases scenarios.

9.3.1.2. Saturated Zone

Ethanol in gasoline will affect the concentrations of BTEX that dissolve into groundwater and the residence time of fuel hydrocarbons in contact with the water table (saturated zone). Although the dissolved equilibrium concentrations of gasoline components—benzene, toluene, ethylbenzene, and xylenes—increase in the presence of high concentrations of ethanol, the 10% ethanol expected to be added to gasoline in California should have only a minor effect on the dissolution of these gasoline components. Relatively hydrophobic compounds, such as xylenes, will be more affected than less hydrophobic compounds, such as benzene. Table 9-2 summarizes

the levels of knowledge on the mechanisms affecting the dissolution of gasoline components in groundwater.

The presence of ethanol in groundwater may alter the processes of sorption and retardation and could contribute to increased benzene plume lengths. As summarized in Table 9-3, the possible impact of these effects is dependent on the quantity of ethanol at the source. For gasoline containing 10% ethanol, these processes will likely be insignificant, whereas for neat-ethanol spills, these processes may become important.

To better assess the overall impact of oxygenated and reformulated gasolines on the length and the longevity of a BTEX groundwater plume, we need a better understanding of the significance of the size, the shape, and the composition of free-product gasoline in contact with the water table. A thorough modeling effort to assess the sensitivity of the overall predictions to these unknown parameters would be an appropriate first step. If the predictions are sensitive to these parameters, then further experimental or modeling studies would be required to improve our ability to estimate them.

9.3.2. Subsurface Biodegradation Processes

The exploitation of natural attenuation processes, within the context of a carefully controlled and monitored site cleanup program, is often the preferred approach to deal with petroleum product releases (National Research Council, 1993). However, current bioremediation and risk-management practices may have to be adapted to the increasing possibility of encountering ethanol as a co-contaminant of a gasoline release. As a first step, additional laboratory and field research is needed to delineate the applicability and limitations of natural attenuation for different release scenarios of BTEX-ethanol mixtures.

Natural attenuation of BTEX contamination relies heavily on anaerobic biodegradation processes (Rifai *et al.*, 1995). In such processes, indigenous microbial communities often degrade BTEX using electron acceptors preferentially in order of decreasing reduction potential (Chapelle, 1993). Sequential depletion of electron acceptors often leads to successive transitions from aerobic to denitrifying, iron-reducing, sulfate-reducing, and methanogenic conditions (see Figure 3-1 in Chapter 3). Biodegradation of fuel alcohols contributes to the depletion of electron-acceptor pools, and this depletion is likely to affect temporal and spatial transitions in electron-acceptor conditions during natural attenuation of releases of ethanol-containing petroleum product. Such geochemical transitions are important to study because they affect both BTEX degradation and migration rates. For example, both the changes in electron-acceptor availability and the presence of easily degradable ethanol could affect catabolic diversity and the relative abundance of specific BTEX-degrading bacteria.

Little is known about the effect of ethanol on microbial population shifts (that is, microbial ecology) and the resulting catabolic diversity. Among the possible effects are enrichment of ethanol-degrading bacteria in relation to BTEX-degrading bacteria, fortuitous enrichment of bacteria that can degrade both ethanol and BTEX compounds, and decreases in populations of certain bacteria as a result of toxicity. Because the efficiency of bioremediation depends, in part, on the presence and expression of appropriate biodegradative capacities of the subsurface microbes, studying the microbial ecology of aquifers contaminated with gasoline-ethanol mixtures could be a fruitful avenue of research. Such studies should address response variability

as a function of a release scenario and site specificity to facilitate risk assessment and remedial action decisions.

To date, little research has been conducted on substrate interactions between BTEX and ethanol. Often, target pollutants are degraded by inducible enzymes whose expression can be repressed when easily degradable substrates (for example, ethanol) are present at high concentrations. Although biodegradation of contaminant mixtures is not very well understood at the biochemical level, preferential substrate degradation appears to be a concentration-dependent phenomenon related to repression of the enzymes needed to degrade the target compounds (Egli *et al.*, 1993). Currently, little is known about the conditions leading to sequential or simultaneous degradation of BTEX in the presence of ethanol. This knowledge gap suggests the need to investigate the concentration-dependent effect that ethanol may have on the induction or repression of enzymes that catalyze BTEX degradation. However, considering that the co-occurrence of BTEX and ethanol may be a short-lived phenomenon relative to the overall duration of a gasoline plume, it is likely that the depletion of oxygen and other electron acceptors resulting from ethanol degradation will be a more important effect of ethanol than the substrate interactions between ethanol and BTEX.

Much of the relevant research to date reflects a reductionist approach to studying the effect of ethanol on natural attenuation. For example, to study the effect of ethanol on specific biodegradation activities, batch studies have often been used that eliminate confounding effects from other variables, such as BTEX and electron-acceptor concentration gradients, as well as mass-transport limitations. Similarly, pure cultures have been used to eliminate confounding effects of microbial population shifts. This work on individual processes generally facilitates hypothesis testing and yields results that are easier to interpret but may do so at the expense of oversimplifying the complex conditions encountered in the field. To determine how ethanol affects BTEX plume dimensions and treatment end points, future research should take on a more holistic approach that considers transport and degradation processes interactively.

Ethanol stimulates microbial processes that may affect aquifer porosity and hydraulic conductivity (for example, biofilm growth, mineral precipitation or dissolution, and nitrogen or methane gas generation). Therefore, it is important to study how the presence of ethanol influences the dynamics of anaerobic microbial communities and related processes that affect the hydraulic and chemical properties of the aquifer. Such research should delineate the conditions that lead to a significant accumulation of volatile fatty acids (VFA, potential degradation products of ethanol), that could decrease the pH to levels that inhibit bioremediation. Emphasis should be placed on evaluating the potential for ethanol-induced methane production to restrict groundwater flow (thus, hindering the replenishment of nutrients and electron acceptors) and to pose an explosion hazard (which raises the possibility of requiring unique corrective action measures).

Because the presence of as little as 1% water can cause “phase separation” of an ethanol-gasoline mixture into an alcohol-rich and a hydrocarbon-rich phase (Bauman, 1999), pure ethanol must be stored at terminals in separate tankage and blended at the distribution terminal just prior to delivery to the end user. Releases of pure ethanol at distribution terminals could magnify the negative effects of many of the issues discussed above. In addition, such releases could occur at sites that are already contaminated with hydrocarbons. Therefore, the effect of

neat-alcohol releases on natural attenuation of pre-existing BTEX and MTBE contamination should also be investigated.

9.3.3. Historical-case Studies

The lack of BTEX and ethanol concentration data at gasohol leak sites is a major knowledge gap. Although 10% gasohol is widely used in Iowa and Nebraska, the ethanol concentrations associated with gasohol releases are typically not measured because ethanol is not a regulated pollutant. There is a perception that no important differences exist between gasoline with and without 10% ethanol, but potential differences have not been evaluated rigorously.

Based on laboratory studies and theoretical considerations, we expect that ethanol may increase BTEX plume length by hindering BTEX biodegradation, enhancing light nonaqueous phase liquid (LNAPL) dissolution, and facilitating BTEX migration due to a decrease in sorption-related retardation during transport. Nevertheless, there is very little information about the subsurface characteristics of ethanol plumes or about the variability of their effect on BTEX fate and transport.

9.3.4. Modeling Uncertainties

9.3.4.1. Benzene Plume Lengths

Several modeling efforts evaluating the behavior of benzene groundwater plumes in the presence of ethanol have been undertaken by a variety of organizations (Chapter 4: McNab *et al.*, 1999; Malcolm Pirnie, Inc., 1998; Ulrich, 1999; Schirmer *et al.*, 1999). These modeling studies indicate that benzene plumes are likely to increase in length under such conditions. The amount of this increase is not determined. Because of the conservative assumptions used regarding unknown transport processes, the models used to forecast benzene plume lengths in the presence of ethanol systematically overestimate plume lengths. Each of these modeling efforts has taken a different approach and has used a different set of simplifying assumptions that may not reflect actual subsurface conditions. A key simplifying assumption that these studies have in common is that the biodegradation rate of benzene is constant in space and in time and for all concentrations of benzene within the plume. This assumption is very conservative; and if benzene biodegradation rates do actually increase downgradient from the ethanol degradation zone, then these modeling predictions significantly overestimate the extent of future benzene plumes. As information from laboratory, field, and historical-case studies becomes available, these simplifying assumptions can be refined, and more accurate and representative forecasts of gasohol-release plumes may be prepared. Improved modeling will aid in the identification of efficient and cost-effective cleanup approaches and resource-management priorities.

9.3.4.2. Impacts to Groundwater Resources

During our analysis of potential groundwater impacts, we used a distance approach combined with known impact probabilities and estimated plume lengths to compare the probabilities of threat to public drinking water wells in California from MTBE or benzene releases (with or without ethanol) from leaking underground fuel tanks (LUFTs). This method provides an important advantage because it allows comparative estimates of potential future impacts between MTBE and benzene in the presence of ethanol. For comparative purposes only, this analysis

develops a modeled estimated baseline for benzene impacts. This baseline estimate is then used to compare potential impacts from MTBE and benzene with ethanol present. The methodology described in Chapter 8 can act as a screening-level approach to identify vulnerable groundwater resource areas.

Based on the results of our analysis, an approximately 20% peak relative increase in public drinking water wells impacted by benzene was estimated if MTBE is replaced by ethanol. The percent relative increase in impacts to public drinking-water wells is estimated to decline from this peak increase at about ten years after the initiation of the use of ethanol. However, the estimated, potential future increase in public wells impacted by MTBE is significantly higher if MTBE were to remain the primary fuel oxygenate. By the conclusion of the first ten-year period, estimated MTBE-well impacts increase by as much as 45% and continue to increase thereafter. This analysis is very conservative, especially with regard to MTBE. Known concentrations of MTBE at LUFT sites were not used in the analysis because only a limited number of LUST sites have a known concentration associated with them.

This approach may be subject to misinterpretations. Because we are examining an absolute probability, there is a concern that the results can be taken out of context. It is important that the relative probabilities be used, using the benzene-alone distributions as the baseline. These estimates are not intended to be used to predict or forecast actual impacts. The results of these estimates are to be used for relative comparison only.

Overall, the average yearly public drinking water source benzene detection rate is under 0.35%. Both toluene and total xylenes have a higher rate, 0.53% and 0.36% respectively. MTBE shows a 1.17% yearly detection rate, much higher than any of the BTEX constituents alone, although similar to the combined BTEX detection rate (1.15%). The evaluation of known detection levels in public water sources is to provide some perspective to the magnitude of benzene or MTBE impacts in the past. Benzene shows a fairly constant detection rate over time, with a slight downward trend when yearly rates are compared. The use of ethanol as a fuel oxygenate would likely increase this detection rate which may stabilize at some higher level. MTBE shows definite upward detection trends; its continued use could, based on the trend results, result in more detections in water sources than benzene within the foreseeable future.

In assessing the probability that MTBE, or benzene with or without the presence of ethanol may affect a drinking-water well or degrade a water supply, several unknowns must be estimated. These include the concentration of benzene, MTBE, or ethanol at a gasoline-release site, the local hydrogeological regime, and the construction of nearby drinking-water wells and their radius of groundwater capture during use. The availability of this data is very limited, and existing data often have significant inaccuracies and errors.

Database location information on public drinking-water wells is often poor. Having accurate locations of public drinking-water wells is important to this effort. Additionally, data on well construction and yield—necessary items to determine a well's intrinsic vulnerability—are not readily available, and collecting that data is costly although recent legislation has made the data more accessible to groups performing environmental assessments.

9.3.4.3. Surface Water Impacts

On the basis of our evaluation and screening-calculations concerning the fate of ethanol in surface-water resources, we conclude that its persistence in surface water will be governed by its biodegradation rate. Screening-level calculations for a scenario that simulates a discrete, seven-day period of watercraft discharges of fuel-borne ethanol (that is, 40 kg/d) to Donner Lake in northern California¹ showed that the peak concentration of ethanol was only 2 µg/L, compared to about 8 µg/L for MTBE under the same release scenario. The difference in levels is due to the elevated biodegradation loss rate assumed to occur for ethanol—compared with the slower volatilization-driven losses for MTBE. For accidental tank-car releases of ethanol to a river or stream, toxic levels of ethanol could occur in the immediate downstream area of a spill. The toxic levels of ethanol would be expected to occur at variable distances downstream from the hypothesized spill with the extent of such toxic concentrations depending on volumetric-discharge conditions. If only a portion of the tank-car inventory were released, the resulting concentrations would also be reduced proportionately.

Aside from the acute toxicity for aquatic species that might be associated with a spill and their associated recovery, it is unlikely that there would be any long-term toxic effects because the ethanol will not persist in water due to its rapid degradation. However, we were only able to identify one study of the biodegradation kinetics of ethanol in a surface water sample (Apoteker and Thévenot, 1983). The key uncertainty with regard to assessments of the impacts of ethanol releases to surface waters is the magnitude of the range of ethanol biodegradation rates.

Rainout of ethanol to surface waters is considered to be more than a factor of 40 greater than for MTBE (by mass per unit-volume), as a result of the large difference between the Henry's law constants for these two compounds. The quantity of ethanol in rainout will only be about 10 µg/L for every part per billion by volume (ppb[v]) of ethanol in air compared to only 0.17 µg/L for MTBE. However, ethanol will biodegrade rapidly in surface water, but MTBE is recalcitrant to such removal.

Nevertheless, for more accurate estimates of the levels of ethanol in rain, temperature-dependent values of the Henry's law constant need to be quantified in laboratory experiments. Compared to ethanol and MTBE, the concentration of isooctane (a representative alkylate) in rain is going to be negligible (estimated to be 0.000036 µg/L per 1 ppb[v] in air). Other isoalkanes are also likely to have very low concentrations in rainwater.

9.3.5. Extracting Ethanol from Aqueous Samples

Having accurate data from field sites is crucial; however, as discussed in Chapter 7 of this volume, ethanol is a small, polar molecule difficult to remove from water. The literature reviewed in Chapter 7 indicates that the technology currently exists to enable researchers to detect ethanol at spill sites. Sufficient methods also exist to determine ethanol at its taste threshold of 50 parts per million (ppm) in water (50 mg/L). However, no routine methods are currently able to detect ethanol below 50 ppb in water. The literature reviewed for this study indicates that either direct injection of an aqueous solution or injection of the headspace above an aqueous liquid can be used to obtain detection limits of 10 ppm or less. The poor extraction

¹ For reference: epilimnetic depth was 8 m, and wind speed was 3 m/s.

efficiency of ethanol from water is the main contributor to its relatively high analytical detection limits. Improved extraction methods will result in better detection limits.

A novel method for ethanol analysis capable of 15-ppb detection limits has been reported. However, this solid-phase microextraction method requires validation before it can be applied routinely to the analysis of environmental samples. Thus, much time and effort must be invested to enable the detection of trace concentrations of ethanol. Until this is accomplished on a routine basis, it will be difficult to monitor effectively the fate and transport of ethanol in the environment.

9.4. Recommendations to Address Knowledge Gaps

9.4.1. Expanded Life-cycle Analysis of the Use of Ethanol and Nonoxygenated Fuel Compounds

A comprehensive life-cycle assessment of ethanol should include the evaluation of release scenarios associated with all stages of its manufacture, distribution, and utilization, including transportation and use of feedstocks and activities at blending centers. This complete analysis would account not only for the mass balance of ethanol in the environment but also for its direct and indirect impacts with respect to issues related to the environment, health, and safety. Accordingly, the objective of a complete life-cycle analysis is to provide a scientifically sound characterization of its input feedstocks and related byproducts as well as their potential impacts. A life-cycle analysis was not prepared for alkylates, but preparing one would also be beneficial in order to understand the nature and magnitude of environmental releases and their impacts.

9.4.2. Additional Field and Laboratory Research

Additional field and laboratory research is recommended as a first step in delineating the applicability and limitations of natural attenuation for the different release scenarios of gasoline containing ethanol.

9.4.2.1. Detailed Field Studies to Refine Conceptual Models

Modeling based on detailed site-specific information is needed. Data from a thoroughly studied field site would refine our conceptual models of critical processes controlling the net fate of gasohol in the subsurface. Because the results of these estimates are largely dependent on the input-parameter probability distributions, historical-case data that better constrain the uncertainty in these probability distributions will improve the predictive capability of any future modeling. The uncertainty inherent in using the complete distribution of benzene concentrations and velocities increases substantially the increase in expected probability for well impacts. Site-specific, maximum concentrations should be used, as opposed to a generic distribution that assumes no knowledge of the specific LUFT site.

A representative site where gasoline containing ethanol has been released should be evaluated in detail, including the collection and analysis of additional soil and groundwater samples needed to support microcosm and column studies. Additional sampling of field sites might be used to provide field verification of microcosm results and increase the number of sites upon which decision-making is based.

Groundwater capture zones should be included in the analysis. The approach we used to evaluate potential groundwater-resource impacts assumes that all plumes move toward a nearby well but with no influence from the well itself. Further probabilistic modeling should be performed to ascertain the sensitivity of this approach to well-capture zones and known groundwater-flow directions.

9.4.2.2. Microcosm and Aquifer Column Studies Using Field Study Materials

Microcosm and associated aquifer column studies are recommended to address knowledge gaps regarding the effect of ethanol on the biodegradation of BTEX compounds. The microcosm studies, which would involve aquifer solids and groundwater from several sites with different histories of fuel contamination, would address the following:

- Microbial ecology/catabolic diversity—assessment of changes in the relative abundance of BTEX-degrading bacteria resulting from exposure to gasoline with and without ethanol under various electron-accepting conditions (based on analysis of DNA that codes for specific aerobic and anaerobic BTEX-degrading enzymes).
- Degradation kinetics—generation of kinetic data (lag periods and degradation rates) for BTEX compounds and ethanol under various electron-accepting conditions in aquifer materials from areas with different histories of gasoline and oxygenate exposure.

The results from such studies will also show whether ethanol metabolism results in marked pH changes in naturally buffered systems as a result of VFA accumulation. The column studies will provide a means to examine whether the kinetic results for the microcosms (for one selected site) are generally consistent with the results in a more realistic, flow-through system. The column studies will also allow researchers to examine how the integrated effects of bacterial metabolism (for example, depletion of electron acceptors and variations in BTEX degradation rates under different electron-accepting conditions) and physical processes (for example, advection and dispersion) result in spatial heterogeneity in degradation processes. The kinetic BTEX and ethanol degradation data could be used in conjunction with existing laboratory data to derive input parameters for predictive modeling.

Although the recommended studies will address some of the most critical knowledge gaps identified during the literature review, they cannot address all knowledge gaps because of time and cost constraints. As discussed earlier, a primary consequence of releases of ethanol-containing gasoline into the subsurface will be the rapid consumption of oxygen and the accelerated development of anaerobic conditions. Long lag times and relatively slow BTEX degradation rates characteristic of anaerobic conditions will constrain the scope of microbiological studies.

9.4.2.3. Historical-case Studies to Develop Statistical Analyses

Additional data should be collected from sites where ethanol-containing gasoline has been released. These data should be used to develop parameter frequency distribution statistics to support the predictive modeling efforts and interpret how the release scenario affects ethanol-plume characteristics. Emphasis should be placed on statistically analyzing BTEX data to determine how ethanol affects the stability and the dimensions of individual BTEX plumes. Such

a survey would provide an integrated picture of the overall effects of ethanol on groundwater pollution from other gasoline components and the natural attenuation of these components. This information would also provide a stronger basis for the selection and operation of appropriate remediation strategies.

A possible outcome of the historical-case analysis would be a statistical comparison of gasoline-release plume lengths at locations where ethanol is present or absent as a fuel component. A reasonable objective is to gather at least 25 cases where ethanol was released as a gasoline component. This population of plume lengths would then be compared to existing historical-case data available for gasoline releases without ethanol.

9.4.2.4. Laboratory Studies to Improve Henry's Law Constants

To improve the prediction of the concentrations of ethanol in rainfall and in surface waters, we recommend that temperature-dependent values of the Henry's law constant be determined in laboratory studies. Additionally, we recommend that further studies be conducted to predict more accurately the biological half-lives of ethanol in different kinds of surface waters in California. This is particularly important because of the important role that rapid natural biodegradation can play for the removal of ethanol from surface waters.

9.4.2.5. Development of Laboratory Analytical Methods

Analysis methods must be improved to meet the data quality requirements contributor to relatively high analytical detection limits. Improved extraction methods will result in better detection limits.

In order to eliminate problems with potential interferences, we recommend that gas chromatographic (GC) separation be used in all future ethanol analyses. There are two practical strategies that can be used for the sensitive detection of ethanol in the presence of interfering compounds. The first is to use the best possible GC procedure to separate ethanol from any interferences and then to detect ethanol with a nonspecific detector, such as a flame ionization detector. The second strategy is to perform a less rigorous GC separation coupled with a detector that would respond specifically to ethanol but would not respond to potentially interfering compounds (for example, an atomic emission detector or a mass spectrometer). Both of these strategies merit careful consideration and comparison.

9.4.2.6. Development of Central Database

More knowledge is required concerning the subsurface environment in California. One of the major unknowns in any hydrogeological investigation is the lack of knowledge of subsurface geology. A great deal can be learned even from the moderate to poor quality of data available in well logs of the California Department of Water Resources. This data should be transcribed into electronic format for use by researchers attempting to draw conclusions on the subsurface.

As part of ethanol studies, we should use GeoTracker and the Geographic Environmental Information Management System (GEIMS) database as a central repository of data. The State Water Resources Control Board (SWRCB) already intends to use this system to help regulators assess sites. Other agencies should be encouraged to supply their data to the system so that

interagency cooperation may be fostered. As Senate Bill 989 (1999)² allows responsible parties to access well construction and other details when under order from a regulatory agency, the associated data for wells in the state of California (lithologic logs, well construction, location, and yield) should be placed in an electronic database to expedite site assessments and decrease costs. This information can also assist in the evaluation of vulnerable groundwater areas as stated elsewhere in the same bill.

Drinking water well and LUFT data already collected by various state organizations should be systematically organized for use in decision analysis. This would permit further comparative analysis of public drinking water wells impacted by gasoline containing ethanol or MTBE from LUFTs. For example, Rempel's 1995 report should be updated to help to understand what factors result in well impacts throughout California.

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² Section 13752 of the Water Code is amended to read: Reports made in accordance with paragraph (1) of subdivision (b) of Section 13751 shall not be made available for inspection by the public, but shall be made available to governmental agencies for use in making studies, or to any person who obtains a written authorization from the owner of the well. However, a report associated with a well located within two miles of an area affected or potentially affected by a known unauthorized release of a contaminant shall be made available to any person performing an environmental cleanup study associated with the unauthorized release, if the study is conducted under the order of a regulatory agency. A report released to a person conducting an environmental cleanup study shall not be used for any purpose other than for the purpose of conducting the study.

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Tables

Table 9-1. Knowledge level for individual properties/mechanisms associated with multiphase flow through the unsaturated zone.

Properties/mechanisms	Knowledge level
Equilibrium composition of the water and hydrocarbon phases	<u>Sufficient information for prediction</u> , but predictive ability has not yet been adequately validated.
Capillary forces—reduction in surface and interfacial tension	<u>Sufficient information for rough, first-order analysis</u> , but significance has not yet been evaluated for this problem.
Effective permeabilities	
– Volume changes as ethanol partitions into water	<u>Insufficient information</u> , extent of volume change understood, but rates and significance are unknown.
– Dehydration and cracking of clay strata	<u>Sufficient information for rough, first-order analysis</u> if typical geological strata can be defined.

Table 9-2. Knowledge level for individual properties/mechanisms associated with the dissolution of gasoline components into groundwater.

Properties/mechanisms	Knowledge level
Equilibrium composition of the two phases	<u>Sufficient information for prediction</u> . Data and modeling available for predicting phase partitioning.
Mechanisms of transport of chemical species through the gasoline pool	<u>Sufficient information for rough, first-order analysis</u> but depends on the size and shape of gasoline pool. Understanding has not yet been adequately applied to this problem.
Mass-transfer rates across the gasoline-water interface	<u>Sufficient information for rough, first-order analysis</u> but depends on the size and the shape of gasoline pool.

Table 9-3. Knowledge level for individual properties/mechanisms associated with the transport of BTEX and ethanol with groundwater.

Properties/mechanisms	Knowledge level
Sorption and retardation	<u>Sufficient information for a rough, first-order analysis</u> . Quality of prediction will depend on ethanol concentrations at the source.
Precipitation of gasoline droplets	<u>Sufficient information for a rough, first-order analysis</u> . Overall impact currently being studied. Quality of prediction will depend on knowledge of ethanol concentrations at the source.

